

AN INVESTIGATION OF POSSIBLE
WAYS TO ENHANCE THE
DEPOSITION OF CALCITE-TYPE COATINGS

JANUARY 1984

Prepared by:
OCEAN CITY RESEARCH CORP.
in Cooperation with
Avondale Shipyards, Inc.

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FOREWARD

This report is the result of one of the many projects managed and cost shared by Avondale Shipyards, Inc. under the auspices of the National Shipbuilding Research Program. The program was a cooperative effort with the Transportation Department, Maritime Administration Office of Advanced Ship Development.

On behalf of Avondale Shipyards, Inc., Mr. John Peart was the Program Manager responsible for technical direction and publication of the final report. Program definition and guidance were provided by the members of the Society of Naval Architects and Marine Engineers Ship Production Committee Panel 023-1 Surface Preparation and Coatings.

The experimental work described in this report took place at the Ocean City Research Corporation laboratory in Ocean City, New Jersey under the direction of Mr. George A. Gehring, Jr.

The research study continued an investigation into the feasibility of applying calcite-type coatings to segregated seawater ballast tanks. It is anticipated that the calcite coating approach could substantially reduce ballast tank coating costs. The overall objective of the National Shipbuilding Research Program is to reduce shipbuilding-related costs in U. S. Shipyards.

EXECUTIVE SUMMARY

The shipbuilding industry has directed much effort toward ways of limiting escalating coating costs. Of special concern with respect to increasing coating costs are segregated seawater ballast tanks. The use of a calcite-type coating instead of a traditional organic-type maintenance coating represents a possible alternative approach for controlling corrosion in the segregated tanks with a substantial savings in cost. As a result, Avondale Shipyards acting on behalf of the Maritime Administration under the National Shipbuilding Research Program authorized the Ocean City Research Corporation to undertake a follow-up laboratory study which continued investigating the feasibility of applying calcite-type coatings to segregated ballast tanks.

The laboratory tests demonstrated the beneficial effect of solution velocity and/or turbulence on the deposition of tenacious calcite films. The work also showed that deposition of calcite films from a quiescent solution can be achieved through the use of a cathodic current in conjunction with the proper solution chemistry. While these films grow to be only 3-4 mils thick in a reasonable time, further laboratory tests indicated their tenacity as well as their thickness can be improved by moderate agitation of the solution. These results suggest the possibility of calcite coating ballast tanks and encourage further research into developing suitable techniques.

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SECTION 1

Conclusions

CONCLUSIONS

1. There exists a threshold level of relative surface velocity and/or turbulence necessary for the chemical deposition of tenacious calcite coatings on steel from a supersaturated calcium carbonate solution.
2. The modification of solution chemistry to optimize zeta potential-related electrostatic forces does not demonstrate any obvious benefits associated with the deposition of calcite coatings from supersaturated calcium carbonate solutions.
3. In a supersaturated calcium carbonate solution, a moderate temperature gradient at the solution/metal interface in itself does not promote significant deposition of calcite.
4. Direct cathodic current deposits a thin film of calcite onto a steel surface from a quiescent solution of 500 ppm Ca^{++} and 150 ppm HCO_3^- . The physical and electrical characteristics of such coatings are superior to that which deposits from seawater under the same conditions. The tenacity as well as thickness of these coatings can be improved by subsequently subjecting the film to a moderately agitated, supersaturated calcite solution.
5. The ability to deposit an initial calcite film under quiescent conditions represents a significant and necessary milestone towards achieving the ultimate goal: deposition of protective calcite films in segregated seawater ballast tanks. Further research appears warranted at this time.

SECTION 2

Introduction

INTRODUCTION

The shipbuilding industry has directed much effort towards ways of reducing the ever-escalating costs associated with protective coatings. The comparatively high costs associated with coating segregated seawater ballast tanks represents a major concern. The problems with staging, abrasive removal, and ventilation in these narrow, limited-access tanks make coating with traditional maintenance coatings (e.g. coal tar epoxy) both difficult and expensive. Therefore, in 1980, the Ocean City Research Corporation under the administration of Avondale Shipyards began an investigation into the possible use of calcite-type coatings as an alternative to the use of traditional maintenance coatings. The concept evolved from technology employed in the waterworks industry where calcite coatings are used for the internal corrosion protection and lining of water mains.

It was envisioned that a calcite coating would be deposited by flooding the tanks with a supersaturated calcite solution. The calcite solution would be prepared by injecting the required chemicals into water obtained from a pierside water source (e.g. fire main) and pumping the solution into the tanks. Injection of the chemicals would be handled from a specially equipped chemical tank truck on the pier.

To achieve adequate corrosion control, it was further envisioned that the use of a calcite-type coating would be supplemented with sacrificial anode-type cathodic protection, the number of required anodes greatly reduced because of the reduction in effective steel surface attributable to the calcite coating. It was also anticipated that, in seawater, the cathodic current supplied by the anodes would have a tendency to deposit a calcareous film thereby reinforcing and maintaining the calcite coating.

The anticipated advantages associated with the calcite coating approach were as follows:

- 1) A significant reduction in tank wall surface preparation.
- 2) Ease of application and maintenance.
- 3) Compatibility with safety and environmental regulations.
- 4) Substantial cost savings.

An initial study (1) demonstrated that tenacious calcite coatings could be deposited from supersaturated solutions as long as there was adequate solution flow/turbulence. Relatively thick (=40 mils) coatings were deposited within 24 hours. Without agitation, however, calcite coating deposition was negligible. Considering the size, location, and geometry of the typical seawater ballast tanks, the practical achievement of significant solution agitation in a tank was considered limited, and thus the feasibility of the calcite coating concept for ballast tanks remained uncertain. Due to the rather significant potential cost savings, MARAD/Avondale authorized the Ocean City Research Corporation to conduct follow-up studies of the calcite deposition process with the effort focused on determining more favorable conditions for calcite coating given the practical limitations imposed by the ballast tank configuration.

SECTION 3

Experimental Approach

EXPERIMENTAL APPROACH

The earlier study sought to demonstrate that the technology used in the waterworks industry for depositing calcite coatings could be readily adapted for use in the segregated ballast tank situation. However, the apparent impracticality of achieving high levels of solution agitation required for calcite deposition using the waterworks industry approach dictated that a more thorough investigation of the calcite deposition process be undertaken. The subject study was directed at developing a more fundamental understanding of the factors limiting calcite deposition as well as determining possible ways of enhancing calcite deposition. Experiments were conducted to: (1) obtain more insight into the threshold velocity/turbulence conditions required for deposition over a reasonable time frame, (2) investigate the effect of solution modification so as to optimize zeta potential effects, (3) investigate possible deposition enhancement associated with a temperature differential, and (4) investigate possible deposition enhancement associated with a combination of solution modification and an applied cathodic current.

Rotating Disk Experiments

Rotating disk experiments were conducted using two different experimental set-ups. First, tests were conducted using a set-up similar to that employed in the earlier study. Steel coupons (SAE 1018, 2" x 2" x 1/8" thick) were rotated in a 10-gallon glass tank containing a supersaturated calcium carbonate solution. The supersaturated calcium carbonate solution was achieved by injecting calcium chloride and sodium carbonate into the tank feedwater stream using chemical metering pumps. The feed rate into the tank was maintained at = 1 gpm, sufficiently high to maintain a constant solution chemistry in the tank. The chemistry of the solution was nominally controlled so as to maintain a pH=10 and a calcium concentration of 180 ppm as CaCO_3 .

Calcium concentrations were determined by an EDTA titration using Eriochrome Blue Black R as an indicator. Total alkalinity was measured by a potentiometric titration with a standard hydrochloric acid. Solution pH was determined using a Chemcadet pH meter (Model 5984-00) calibrated with NBS traceable buffer solutions of pH 7.00 and 10.00. Rotating coupons were exposed for different time frames and at selected speeds, ranging between 240 and 350 rpm.

In order to better characterize deposition/time behavior as well as gain more of an insight into the nucleation and growth stages of the process, additional experimentation was conducted where seven coupons were rotated simultaneously on a common shaft at a speed of 300 rpm (previous experimentation showed calcite deposition would occur rapidly at this speed). One coupon was removed for inspection after an exposure time of 1/2, 1, 2, 3, 4, and 11 hours.

Another set of experiments was conducted using a 1-foot diameter circular disk rotated in a 50-gallon tank of supersaturated calcium carbonate solution. The test solution chemistry was maintained in a fashion similar to the above-reported procedures. Using a synchronous motor and appropriate gear reduction, the disk was rotated at exactly 60 rpm, providing a velocity of 3.1 ft/sec at the edge of the disk. The disk was fabricated from steel plate (SAE 1018, hot-rolled) and had beveled edges in order to limit turbulence on the bottom surface. The plate was acid descaled and then finished with 220 grit sandpaper. Figures 1 and 2 show the test set-up.

Modification Of Solution Chemistry To Optimize Zeta Potential Effects

In considering what might be done (in terms of modifying solution chemistry) to improve calcite deposition under quiescent conditions over that observed in the previous study, it was

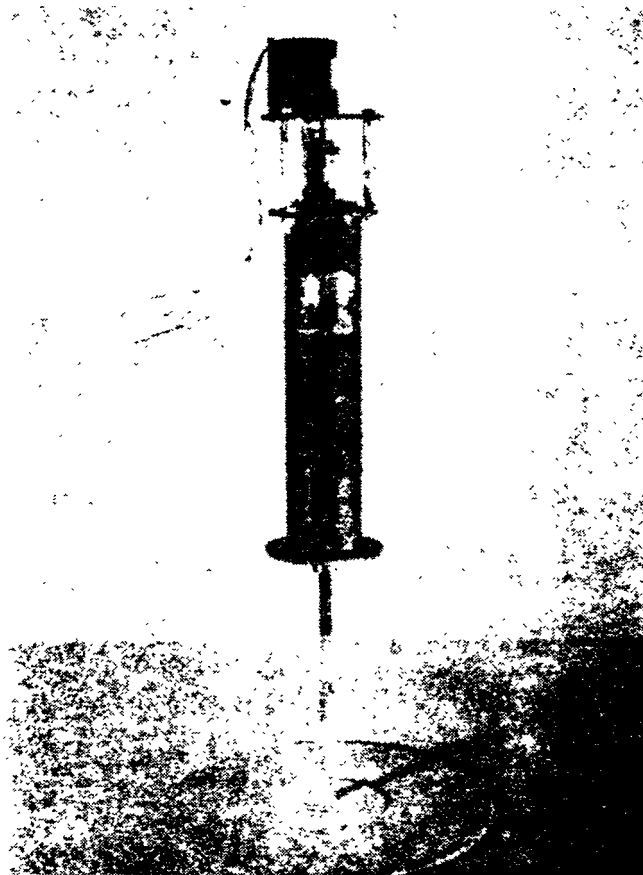


FIGURE 1 - Rotating Disk Apparatus

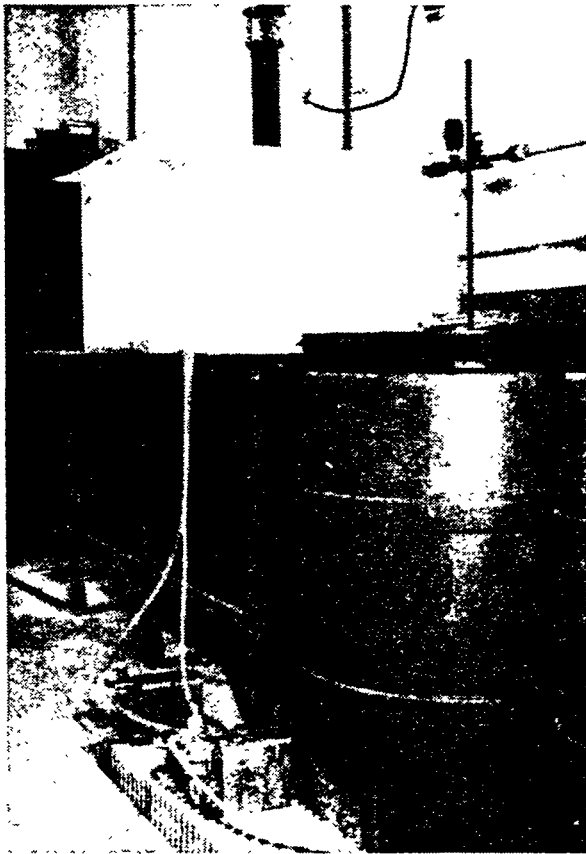


FIGURE 2 - Tank Set-up for Rotating Disk Immersed in Supersaturated Calcite Solution. (Also shown are chemical supply tanks and metering pumps.)

decided to investigate whether deposition would be enhanced if the solution chemistry were adjusted to maximize the zeta potential difference between calcium carbonate and iron oxide (presumed to be the substrate on which deposition actually occurs). The zeta potential occurs as a result of the charged double layer present on the surface of a particle in solution. The magnitude and polarity of the zeta potential are dependent on a number of parameters, with the most important being solution pH. Theoretically, there should be a pH range or pH "window" where the zeta potential of calcium carbonate will be of opposite polarity (opposite surface charge) to that of the steel surface presumably covered with a thin layer of iron oxide. The isoelectric point, the pH at which the sign of the zeta potential changes from positive to negative, is approximately 7.4 for iron oxide and 9.5 for calcium carbonate. Between these pH values, the respective zeta potential polarities of iron oxide and calcium carbonate will be opposite and therefore, an attractive electrostatic force should exist. Figure 3 shows graphically the pH "window" where theoretically there should be an attractive electrostatic force. It is of interest to note that most of the earlier studies were conducted at solution pH's higher than 9.5 where a repulsive electrostatic force would be expected.

To investigate possible zeta potential effects on calcite deposition, steel coupons were exposed to varying solution chemistries. Three solution parameters were judged to be important in developing the solution chemistry test matrix: (1) the solution pH, (2) the calcium carbonate supersaturation ratio, and (3) the carbonate to calcium ion ratio. The range over which each of the respective parameters was investigated follows:

pH : 8.0 to 9.0

CaCO₃ supersaturation ration : 10 to 100

CO₃⁻⁻/Ca⁺⁺ ratio : 0.5 to 2.0

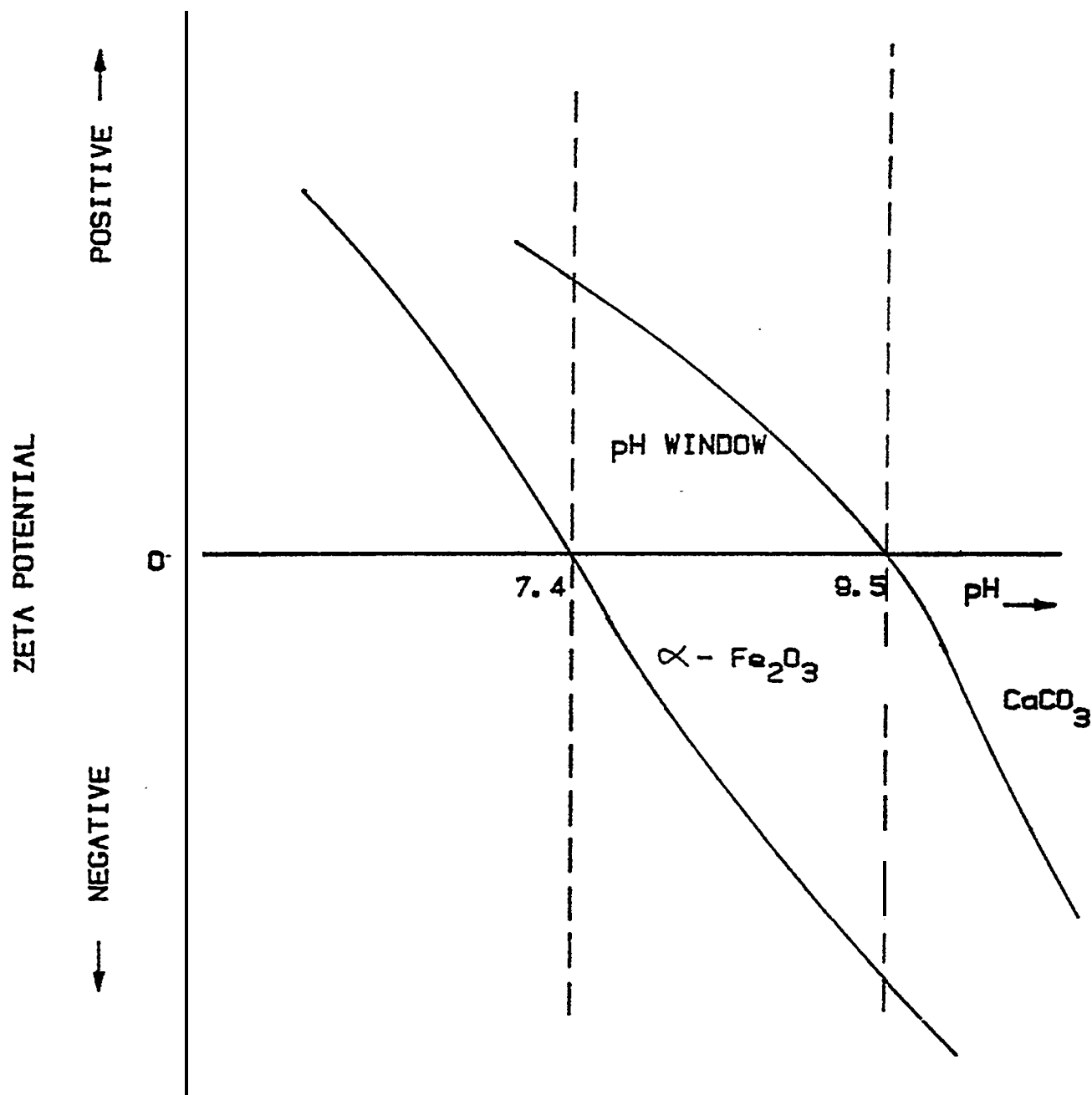


FIGURE 3 - Graphical Representation of the pH "Window" Associated with Zeta Potential. (A region of attractive electrostatic forces between calcite and iron oxide.)

Table I shows the full test matrix.

A computer program was utilized to calculate the proper weights of chemicals that had to be added to solution in order to achieve the desired values associated with the above-listed parameters. Reagent grade calcium chloride dihydrate and sodium bicarbonate were used in preparing the test solutions. When necessary, hydrochloric acid or sodium hydroxide were added to correct solution pH.

The steel coupons were cold-rolled, SAE 1010 steel, 3" x 5" x 0.032" thick*. The coupons were suspended in individual test cells containing the different test solutions. The test cells consisted of sealed, 2-liter plastic containers. The coupons were suspended from the top of the container by an electrical lead wire. The lead wire provided an electrical contact to the coupon in order to make corrosion potential measurements. The container lids included an additional port to permit insertion of a reference electrode or chemical sampling. Solution chemistry was monitored by methods previously described. The potential measurements were made using a Data Precision Model 258 digital multimeter and a saturated calomel reference electrode.

The solution temperature was maintained constant at $25^{\circ}\pm 1^{\circ}\text{C}$ by immersing the test cells in a constant temperature water bath. The coupons were exposed for a 24-hour period. At the end of the 24-hour period, the coupons were examined under a microscope (Unitron 7941 Metallograph) up to a magnification of 800X to determine the extent of calcite nucleation. More in-depth examinations were made using a JEOL JSM-50 scanning electron microscope.

* Q-panels as supplied by the Q-Panel Company, Cleveland, Ohio.

TABLE I - Test Matrix For Investigating Zeta Potential Effects

<u>TEST NO.</u>	<u>SATURATION INDEX</u>	<u>SOLUTION pH</u>	<u>CO₃-- / Ca⁺⁺</u>
1	10	8.0	0.5
2	10	8.5	0.5
3	10	9.0	0.5
4	50	8.0	0.5
5	50	8.5	0.5
6	50	9.0	0.5
7	100	8.0	0.5
8	100	8.5	0.5
9	100	9.0	0.5
10	10	8.0	1.0
11	10	8.5	1.0
12	10	9.0	1.0
13*	50	8.0	1.0
14	50	8.5	1.0
15	50	9.0	1.0
16*	100	8.0	1.0
17	100	8.5	1.0
18	100	9.0	1.0
19	50	8.0	2.0
20	100	8.0	0.5

* Solution chemistries chosen for 2-week tests.

In addition to the 24-hour tests, longer tests were conducted over a 2-week period on those solution chemistries that appeared promising based on the 24-hour results. The coupons were exposed continuously in solutions that were refreshed daily.

Temperature Differential Experiments

It is well known that calcite-type scaling occurs on the cold side of boiler tubing due to an inverse relationship between temperature and calcium carbonate solubility. As a result, the possibility of using a temperature differential between the steel surface and solution to enhance deposition was investigated.

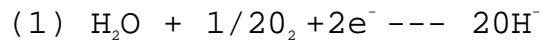
The experiments were carried out in a test cell containing a U-tube through which hot water passed. The U-tube was immersed in the test solution. The hot water to the U-tube was pumped and recirculated from an insulated, thermostatically-controlled cell which maintained the hot water at the desired temperature. A thermometer located in the bulk of the hot fluid indicated the hot side temperature. The cell containing the U-tube had various ports allowing for the continuous feed of fresh test solution which kept the bulk solution chemistry constant as well as the test solution cool. The test solution chemistry was maintained in a fashion similar to the rotating electrode experiments. Solution chemistry, electrochemical potentials, and bulk solution temperature were monitored throughout the tests. The tests investigated two temperature differentials as measured between the test solution and hot water -- 45°C and 55°C.

In rotating electrode experiments in highly supersaturated test solutions, hard calcite coatings developed on a heating element placed in the solution. As a result, a similar solution chemistry (pH=10, $\text{Ca}^{++} = 180$ ppm as CaCO_3) was included in these experiments. The other solution chemistry selected for testing was a solution of pH=8.2 and a high calcium concentration ($\text{Ca}^{++} = 1250$ ppm as CaCO_3). The tests were conducted over 5-day

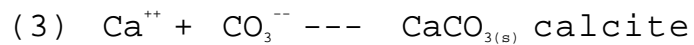
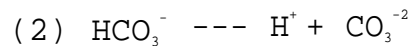
periods. At the end of the test periods, the tubes were inspected in order to characterize the extent of calcite deposition.

Solution Modification In Conjunction With An Applied Cathodic Current

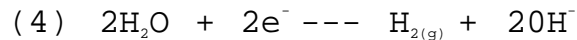
Cathodic current causes the precipitation of calcite by creating a local region of high pH at the metal surface. The high pH is created by the reduction of dissolved oxygen as presented by equation (1).



The result of this reaction is to shift the bicarbonate/carbonate equilibrium (equation 2) to the right thereby supersaturating the interface and promoting precipitation (equation 3).



Hydrogen gas evolution occurs at higher cathodic current densities (equation 4)



In the previous study, attempts to stimulate or enhance calcite deposition by applying a cathodic current were unsuccessful. However, in the previous study, the effect of cathodic current was only investigated in test solutions of high pH and comparatively high supersaturation. Knowing that steel surfaces cathodically protected by magnesium in seawater develop calcite-like deposits, another attempt was made using a test solution of distilled water containing calcium ion and bicarbonate ion in concentrations similar to that found in natural seawater (500 ppm Ca^{++} and 150 ppm HCO_3^-) .

Initially, experiments were carried out using 1" x 3" SAE 1010 steel coupons that were coupled to a magnesium anode through an electrical lead wire and immersed in a solution similar to that described above. Later experiments used smaller steel coupons (1 square centimeter) cast into an epoxy base. A lead wire soldered to the back of the coupon provided an electrical contact. Tests were carried out at both constant potential and constant current. For the constant potential tests, an Aardvark Model PEC-AM was used while a simple resistive network coupled to a voltage source was used for the constant current tests. Electrochemical potential and polarization measurements were made throughout the tests.

For the most part, the test solution chemistry was similar to that described above although some solutions having a different pH, different calcium, or different bicarbonate concentration were also investigated. Reagent grade calcium chloride dihydrate and sodium bicarbonate were used in all experiments except those using 10,000 ppm Ca^{++} in which a desiccant grade anhydrous calcium chloride was used. Coupons were inspected microscopically as appropriate during the different test runs. Film thicknesses were estimated by measuring the distance between bare substrate and coating peaks using a microscope with a calibrated focusing knob. Higher magnification, better depth-of-field examinations were conducted using a scanning electron microscope. Depending on each experiment, the test durations varied between 15 minutes to 3 weeks. Table II presents the test matrix.

TABLE II - Test Matrix For Investigating The Effects Of
Cathodic Current Used In Conjunction With
Various Solution Chemistries

<u>TEST NO.</u>	<u>ppm Ca⁺⁺</u>	<u>ppm HCO₃⁻</u>	<u>pH</u>	CONSTANT		<u>DURATION</u>	<u>STIRRED</u>
				<u>POTENTIAL</u> <u>volts vs SCE</u>	<u>/ CURRENT</u> <u>uA/cm²</u>		
1	500	150	7.8	-1.5 (Mg anode)	--	5 days	no
2	Natural Seawater		8.0	-1.5 (Mg anode)	--	5 days	no
3	500	150	7.8	-0.905	--	2 days	no
4	500	150	7.8	--	30	1 day	no
5	500	150	3.5	-1.05	--	1 day	no
6	500	150	5.0	-1.05	--	18 hours	no
7	500	150	5.0	-1.05	--	5½ days	no
8*	500	150	7.8	-1.3	--	21 hours	no
9	500	150	7.8	-1.2	--	4 days	no
10**	500	150	7.8	-1.05	--	4 days	no
11	5000	150	5.0	-1.05	--	2½ days	no
12	500	150	7.8	-1.05	--	3 days	yes

* Using coupon from test #7.

** Using coupon from test #9.

TABLE II - Continued

<u>TEST NO.</u>	<u>ppm Ca⁺⁺</u>	<u>ppm HCO₃⁻</u>	<u>pH</u>	<u>CONSTANT</u>		<u>DURATION</u>	<u>STIRRED</u>
				<u>POTENTIAL</u> <u>volts vs SCE</u>	<u>/ CURRENT</u> <u>μA/cm²</u>		
13***	500	150	7.8	--	50	1 day	no
14	Natural Seawater		8.0	-1.03 (Zn anode)	--	3 weeks	yes
15	10000	150	7.8	-1.03 (Zn anode)	--	3 weeks	yes
16	10000	150	7.8	-1.5 (Mg anode)	--	3 weeks	yes

*** Followed by exposure to a slightly agitated supersaturated calcite solution.

S E C T I O N 4

Results and Discussion

RESULTS AND DISCUSSION

Rotating Disk Experiments

The rotating disk experiments reconfirmed that with sufficient agitation or velocity adherent calcite coatings could be built up quite rapidly in supersaturated calcium carbonate solutions. Figures 4a. thru 4f. illustrate the growth process for a square disk rotated" in a highly supersaturated calcite solution. After 1/2 hour, a grayish layer appears as the initial growth on the disk surface (Figure 4a.). This layer is quite strongly bonded to the surface and represents initial crystal nucleation. This layer forms a base for future growth. Figure 5a. shows this initial layer as observed with a scanning electron microscope. Energy dispersive X-ray (EDAX) analysis indicated that calcium and iron are the major surface elements (Figure 5b).

After 1 hour, deposition of larger calcite crystals can be observed on the coupon edges. With time, the deposition progresses inward toward the center of the coupon. After 11 hours (Figure 4f.), a coating approximately 40 roils in thickness had developed uniformly over the coupon surface.

A significantly slower growth rate was observed in the rotating disk experiments using a 1-foot diameter circular disk. In order to obtain a coating 40 roils thick, the disk had to be spun for 48 hours in a solution of similar chemistry. Figure 6 shows the typical surface appearance after 48 hours. The coating on the surface was quite hard from a radius of 4 inches outward. Less than 4 inches from the center, the coating was not as tenacious or well bonded. Moving toward the center, the coating thickness decreased from 40 roils at 4 inches from the center to 25 mils at 1 inch from the center. At the very center area of the disk, only a grayish layer, apparently the initial iron/calcite layer, existed. This layer measured 7 roils thick. As

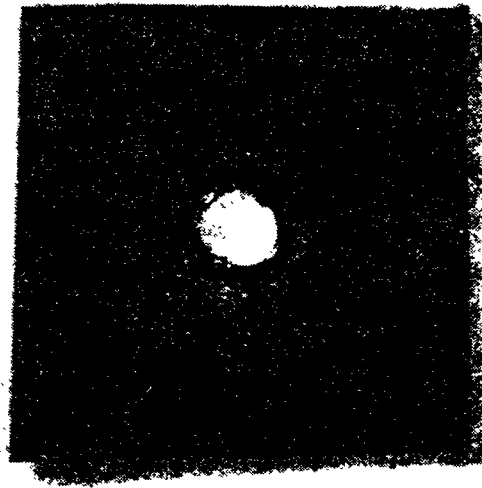


FIGURE 4a - Appearance of a Rotating Square Electrode
After 1/2 Hour Exposure.



FIGURE 4b - Appearance of a Rotating Square Electrode
After 1 Hour Exposure.

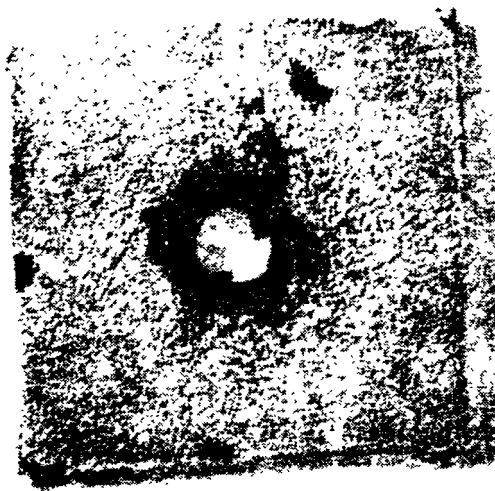


FIGURE 4c - Appearance of a Rotating Square Electrode
After 2 Hours Exposure.

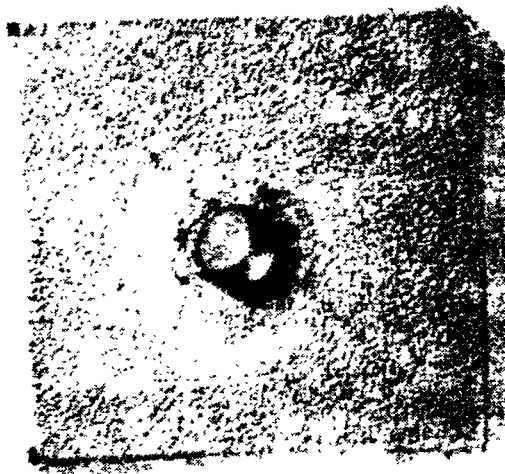


FIGURE 4d - Appearance of a Rotating Square Electrode
After 3 Hours Exposure.



FIGURE 4e - Appearance of a Rotating Square Electrode
After 4 Hours Exposure.



FIGURE 4f - Appearance of a Rotating Square Electrode
After 11 Hours Exposure.

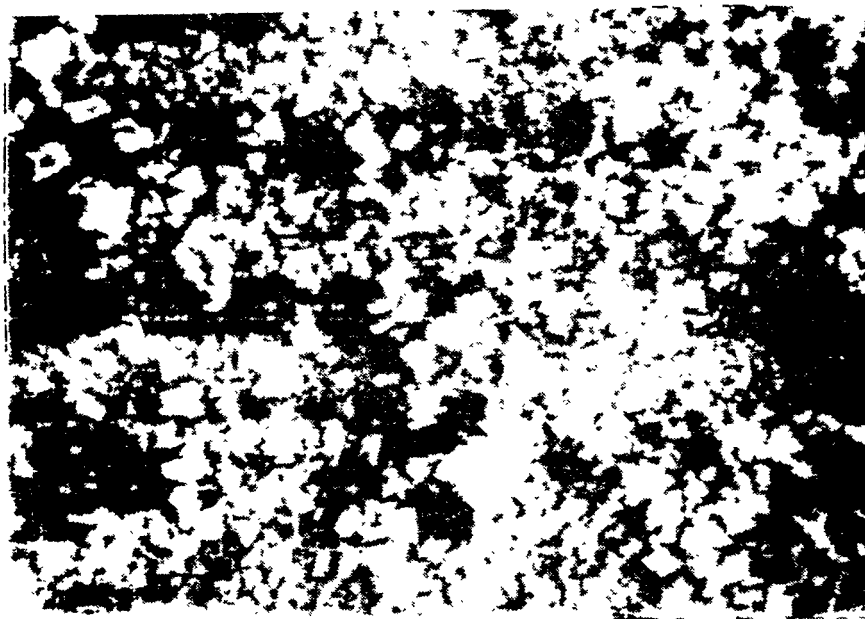


FIGURE 5a - SEM Photomicrograph of the Surface of the Rotating Square Coupon Shown in Figure 4a (3 0 0 X) .

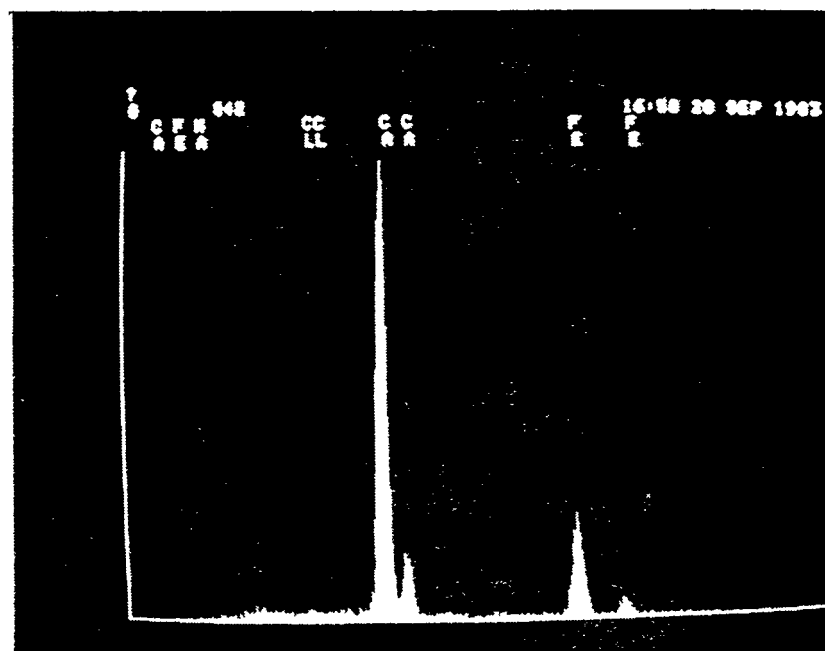


FIGURE 5b - EDAX Analysis of the Surface

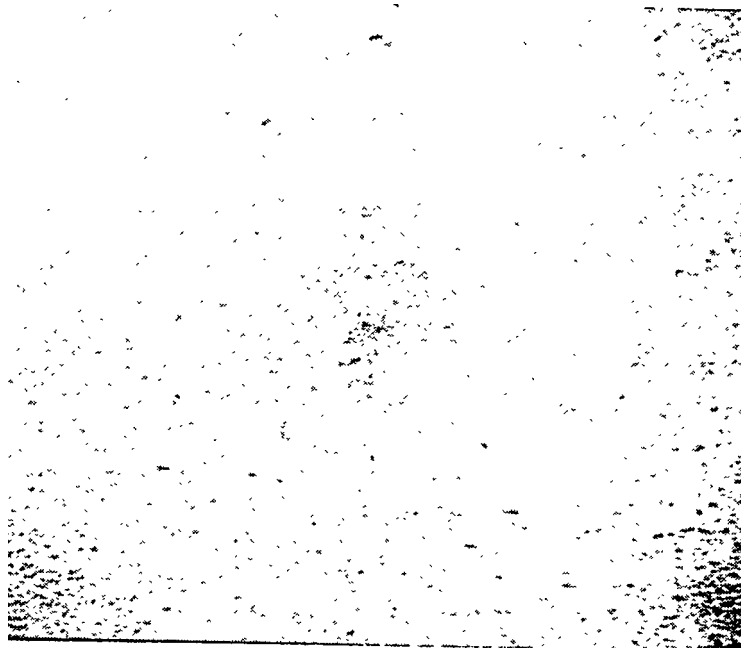


FIGURE 6 - Surface Appearance of the Rotating Circular Disk
After 40 Hours Immersion in a Highly Super-
saturated Calcite Solution.

for the square coupons, the coating process began at the disk edge and proceeded towards the center.

During the rotating disk experiments, the tank walls (plastic) of the 50-gallon container became coated with a calcite layer. The area of the tank wall subjected to impingement from the makeup solution developed an exceptionally hard and thick coating within 24 hours. The impingement velocity was ≈ 5 ft/sec. Figure 7 shows this area. Figure 8 shows the general appearance of the tank walls not subjected to direct impingement. While the coating is not tenacious in these areas, it does extend evenly into the corners.

Solution movement or agitation does not appear to be a necessary factor in the initial or nucleation stage of the deposition process. On the 1-foot circular disk, the initial grayish layer was evident even at the very center. Calcite deposition was also observed on the walls of the plastic tank even in areas of almost zero relative surface velocity (the corners). These observations suggest that calcite crystals either nucleated in the saturated solution and precipitated on the exposed substrate surfaces or calcite crystals actually nucleated at the substrate/solution interface because of more favorable surface energy conditions.

While solution movement or agitation seems to have little influence on crystal nucleation, it does appear to have a strong affect on both the growth stage of the deposition process and the bonding/structural characteristics of the resulting film. The lack of any calcite coating other than the initial nucleation layer at the center demonstrates the influence of solution movement on growth. Furthermore, the 1-foot steel disk rotated at 60 rpm exhibited a thinner, less adherent, and structurally weaker coating at points less than 4 inches from the center. This phenomena was observed consistently throughout the test runs. At a radius of 4 inches, the nominal surface velocity is

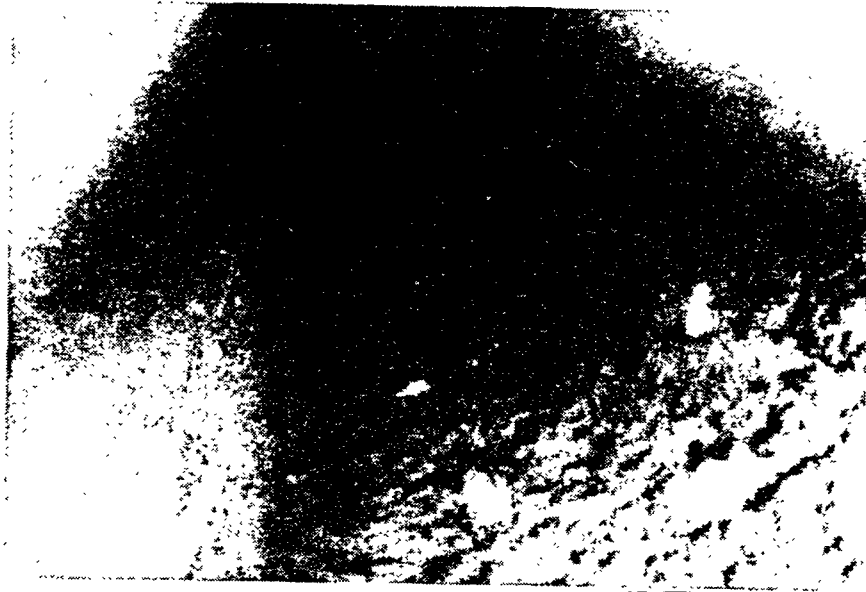


FIGURE 7 - Area of Impingement of Calcite Feed Solution on the Wall of the 50-Gallon Tank. (Arrow indicates region of an exceptionally hard coating.)



FIGURE 8 - General Appearance of Tank Walls Showing Uniform Calcite Coating Deposition in the Corners.

2ft/sec. McCauley (2) reported a marked decrease in the quality of calcite films deposited at velocities less than 2 ft/sec.

Qualitative examination of the rotating square coupons also suggested that the tenacity of the coating improved towards the edges where flow velocities and turbulence were highest. Because of the different configuration of the test set-up and the different specimen geometry (square vs. round), it is difficult to compare directly the results on the square coupons with results of the rotating circular disk experiments. But a general comparison suggests that the increased turbulence promotes faster growth as well as a more tenacious coating. The tendency to have more adherent crystals towards the edges of the square coupon indicates that the crystal morphology at the electrode perimeters may be different; highly turbulent conditions may lead to tenacious coatings because all crystals have to be well bonded in order to resist being washed away. A different crystalline morphology may also be the reason behind the more rapid crystal growth at the electrode perimeters, (i.e. it presents a base more conducive to quick growth).

Another possible advantage of a moving or agitated solution over that of a stagnant solution in promoting calcite growth can be reasoned as follows. For both cases, at the metal/solution interface, the crystals on the surface will be in equilibrium with the solution (the interface concentration is that of saturated solution). Moving away from the interface, two different possibilities exist. Under flowing conditions, a supersaturated solution exists just beyond the interface as a result of the solution movement (i.e. the solution which has just deposited calcite on the surface is continually refreshed). Under stagnant conditions, the solution next to the interface deposits calcite on the surface and becomes undersaturated. Further calcite deposition requires re-saturation of the solution adjacent to the interface. Under stagnant or quiescent conditions, this occurs

by diffusion of the reacting species into the depleted or under-saturated region, which is a comparatively slow process.

Modification Of Solution Chemistry To Optimize Zeta Potential Effects

The experiments investigating the possible optimization of zeta potential effects "by solution modification in order to enhance deposition under quiescent conditions did not yield promising results. After a 24-hour period, no significant calcite nucleation was observable on any of the test coupons exposed to the various solution chemistries included in the test matrix (Table I). After 2 weeks, only thin coatings consisting of intermingled rust and calcite were evident. Figure 9 shows the typical appearance after a 2-week exposure.

Although the experiments in this phase of the study did not provide any obvious clues as to how to enhance the deposition process under quiescent conditions, there were some interesting results worth noting. Some test panels were observed to passivate within 24 hours when exposed to solutions of high sodium bicarbonate concentration, low calcium chloride concentration, and a bulk solution pH of 8. Potentials approximately 700 millivolts noble to the typical corrosion potential of steel were observed, and full cathodic-anodic polarization scans revealed the existence of a very large passive region. These test panels showed no signs of rusting at all whereas all panels that remained active rusted within twenty-four hours. Inspection with an optical microscope indicated the presence of very small particles on the surface. Electron microscope scans show the surface to be partially covered with crystal growth as shown in Figure 10a. EDAX analysis of the surface crystals indicated the presence primarily of sodium, chlorine, and iron (Figure 10b).

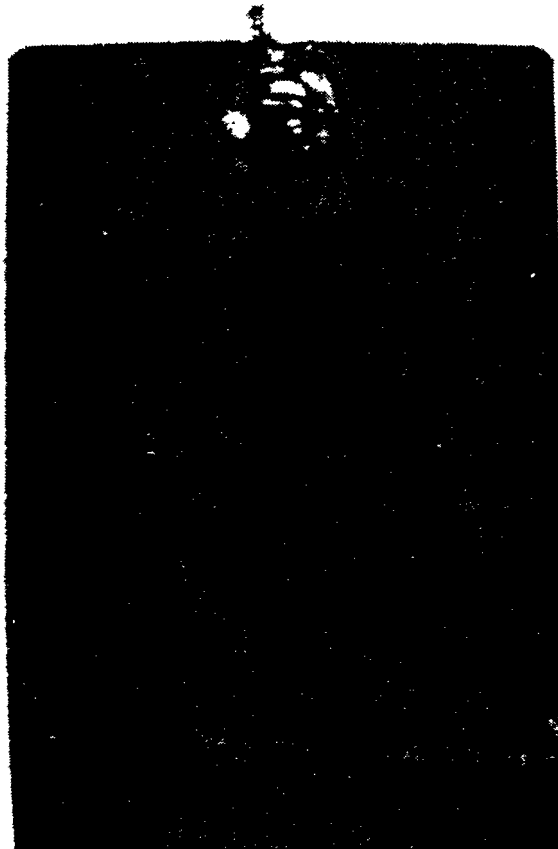


FIGURE 9 - Typical Appearance of Q-Panel after 2 Weeks
Immersion in Supersaturated Calcite Solution
(pH = 8, S = 50, R = 1.0).



FIGURE 10a - SEM Photomicrograph of Surface of a Steel Panel that Passivated Within 24 Hours When Exposed to a Supersaturated Calcite Solution (pH = 8, $S = 5.0$, $R = 1.0$), 300X

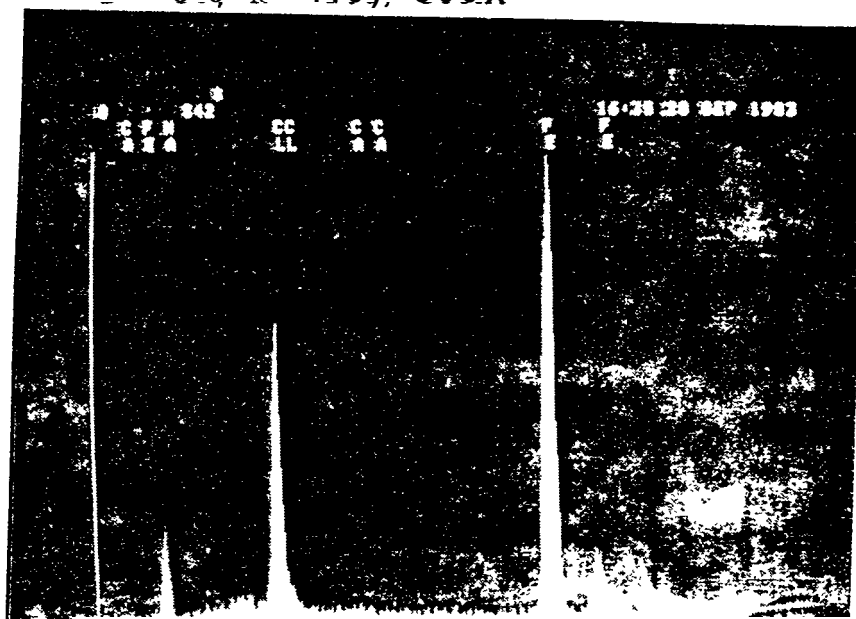


FIGURE 10b - EDAX Analysis of a Portion of the Crystal Structure Shown in Figure 10a.

In one instance, a growth similar in appearance to that shown in Figure 10a was observed on the surface of a panel exposed in a test solution for two weeks. Interestingly, these panels had remained at active potential values (-700mv vs SCE) for the first week of testing and then passivated as evidenced by their corrosion potential shifting to -60mv vs SCE. The crystal growth could be seen without magnification (the white trace in Figure 9). Figure 11 shows this crystal growth at a magnification of 300X. Identification has not been made of the crystals at this time. Also their role, if any, in the passivation of the coupons was not determined.

Temperature Differential Experiments

The temperature differential experiments at 45° and 55°C both developed an apparent soft calcite coating intermingled with rust on the U-tube surface. The top surface of the coating was easily washed away, leaving a more adherent layer of about 2 mils in thickness. Figure 12 shows the appearance of this layer on the U-tube, which developed over a 1-week exposure in a solution of pH=8.3, Ca^{++} =1250 ppm, and At of 55°C.

The two temperature differentials investigated (45 and 55°C) cause approximately a factor of 2 reduction in calcite solubility at the warm surface. While this does promote calcite deposition, the hard coating that is observed in practice on boiler tubes and was observed on the heating element immersed in a highly supersaturated test solution in another phase of the study did not develop. The temperature at the surface of a boiler tube might be as high as 115°C which would result in approximately a factor of 4 reduction in calcite solubility (given a cooling water bulk temperature of 25°C). However, temperature differential is not the only factor affecting calcite deposition on the surface; nucleate boiling plays a role. As heat rapidly transfers through the tube wall, the cooling water cannot conduct the heat away fast enough and thus "flashes" creating a vapor column and leav-



FIGURE 11 - Photomicrograph of the White Trace Observed on the Bottom of the Q-panel Shown in Figure 9 (300X) .

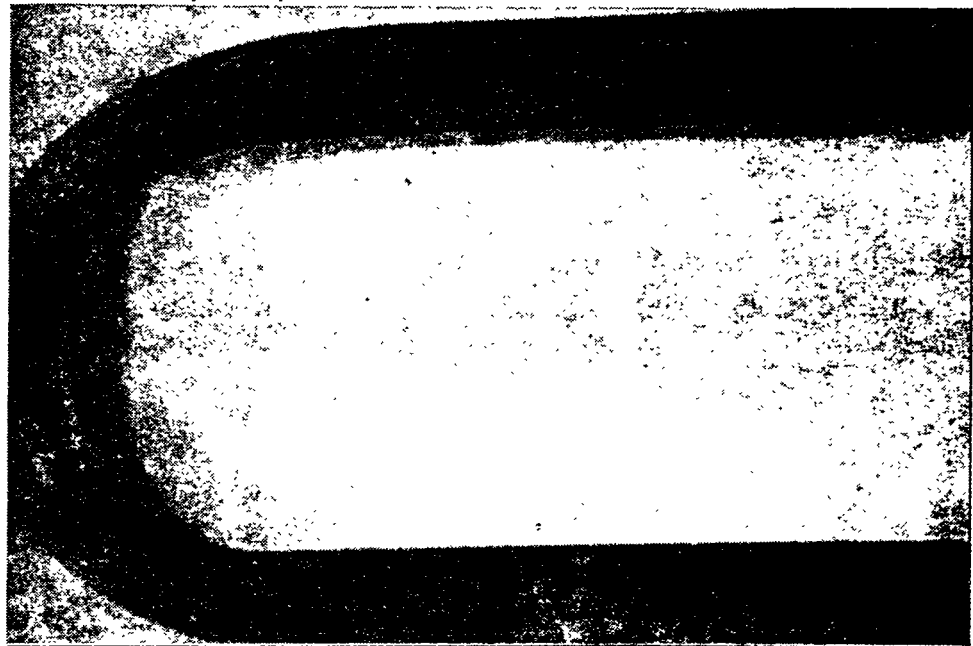


FIGURE 12 - Appearance of the U-tube after a One Week Exposure to a Supersaturated Calcite Solution (pH = 8.3, Ca^{++} = 1250 ppm, HCO_3^- = 300 ppm, ΔT = 55°C) .

ing any dissolved solids behind on the tube surface. A similar situation might be expected on the 1000 watt heater element that developed a hard coating. It should be pointed out that it is also this factor of nucleate boiling which creates holes and crevices in the calcite coating on boiler tubes, resulting in areas susceptible to enhanced corrosion.

Cathodic Protection/Solution Modification Experiments

Figure 13 shows the appearance of a coupon after immersion for 5 days in a calcite solution (500 ppm Ca^{++} , 150 ppm HCO_3^-) having a bulk solution pH of 7.8. The coupon was maintained at a constant potential of -1.5 volts (vs. SCE) by coupling to a magnesium anode. Figure 14 shows the appearance of a coupon exposed similarly in natural seawater. The coatings that developed on the coupons were quite brittle and loosely bonded. Also, hydrogen evolving on the surface as a result of the cathodic current flow was observed to blister and disbond the calcite coating at different spots.

Based on the above-described results, another series of experiments were initiated using 1 cm^2 steel coupons controlled at selected constant potentials or constant currents. First, a coupon was exposed in the same calcite solution described previously (pH=7.8, Ca^{++} =500 ppm, HCO_3^- =150 ppm) and maintained at a constant potential of -0.905 volt vs. SCE. This potential was selected because hydrogen evolution was expected to be minimal at this potential level. Initially, the cathodic current density to the coupon was =40 $\mu\text{A}/\text{cm}^2$. Within two days the current density dropped to less than 1 $\mu\text{A}/\text{cm}^2$. The test was then stopped and the coupon removed for examination. Inspection of the surface revealed a tightly adherent, rather uniform crystalline film. The film thickness averaged 0.9 mils. This surface is shown in Figure 15a. An EDAX analysis (Figure 15b) confirmed that calcium

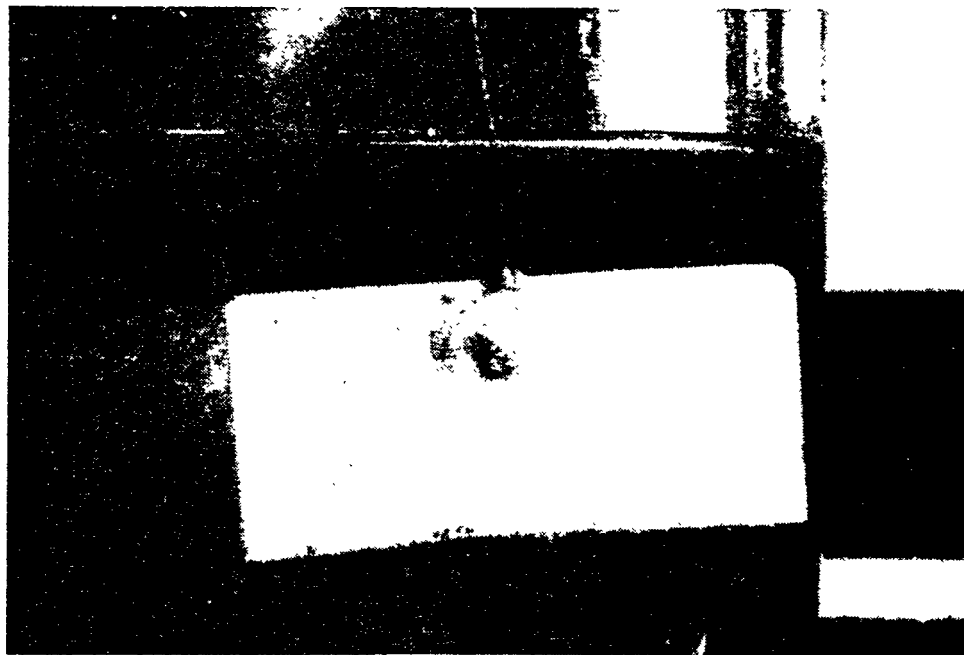


FIGURE 13 - Appearance of Steel Coupon after 5 Days Coupled to a Magnesium Anode and Immersed in a Solution of 500 ppm Ca^{++} as Ca, 150 ppm HCO_3^- , and pH = 7.8.

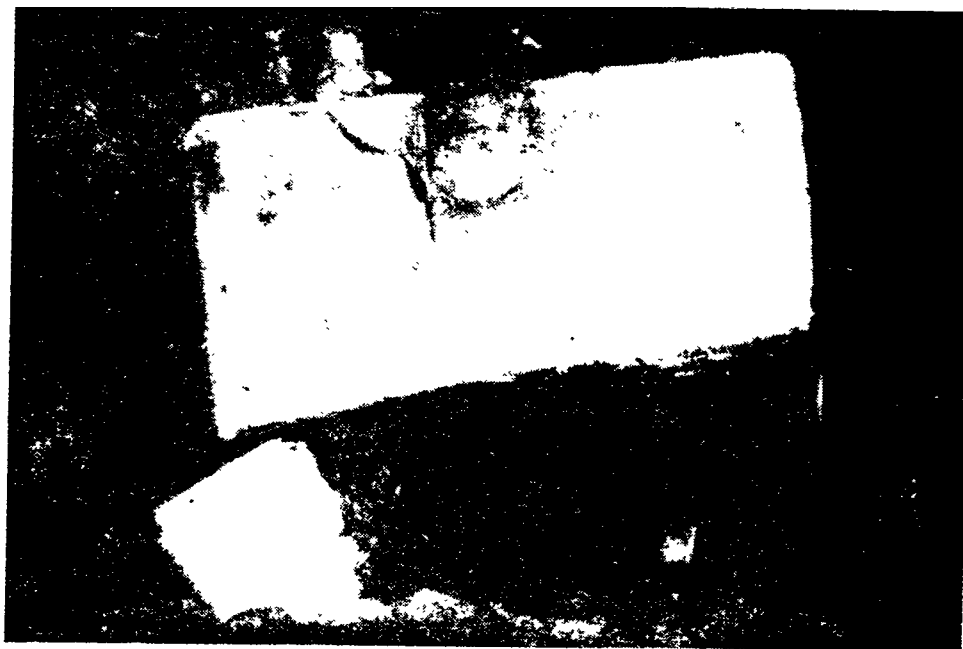


FIGURE 14 - Appearance of Steel Coupon after 5 Days Coupled to a Magnesium Anode and Immersed in Natural Seawater.



FIGURE 15a - SEM Photomicrograph of the Surface of a 1 cm² Steel Coupon Held at -0.905 Volt vs. SCE for 2 Days in a Solution of 500 ppm Ca⁺⁺, 150 ppm HCO₃⁻, and pH = 7.8 (300X).

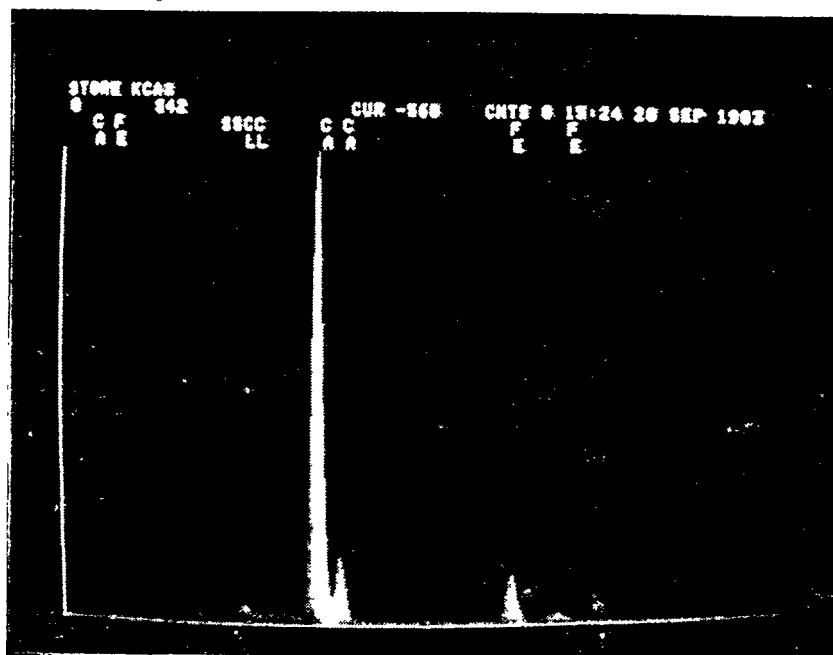


FIGURE 15b EDAX Analysis of the Surface Shown in Figure 15a.

was the predominant surface element, indicating the film was primarily CaCO_3 . The decrease in current flow to the coupon is believed attributable to the development of this calcite film on the surface.

A decrease in cathodic current density will generally be accompanied by a corresponding decrease in calcite film growth rate under the subject test conditions. Therefore, it was decided to conduct a test with the current density held constant rather than potential. A test under similar conditions was then run at a constant current density of 30 uA/cm^2 for 24 hours. Initially, the coupon potential was -0.840 volt (vs. SCE). As the test progressed, the potential shifted in an active "direction, reaching a final value of -1.23 volts. The active potential shift was caused by the development of an electrically resistive crystalline film on the coupon surface. The shift in potential to such an active value resulted in hydrogen evolution which disrupted the calcite film in isolated areas.

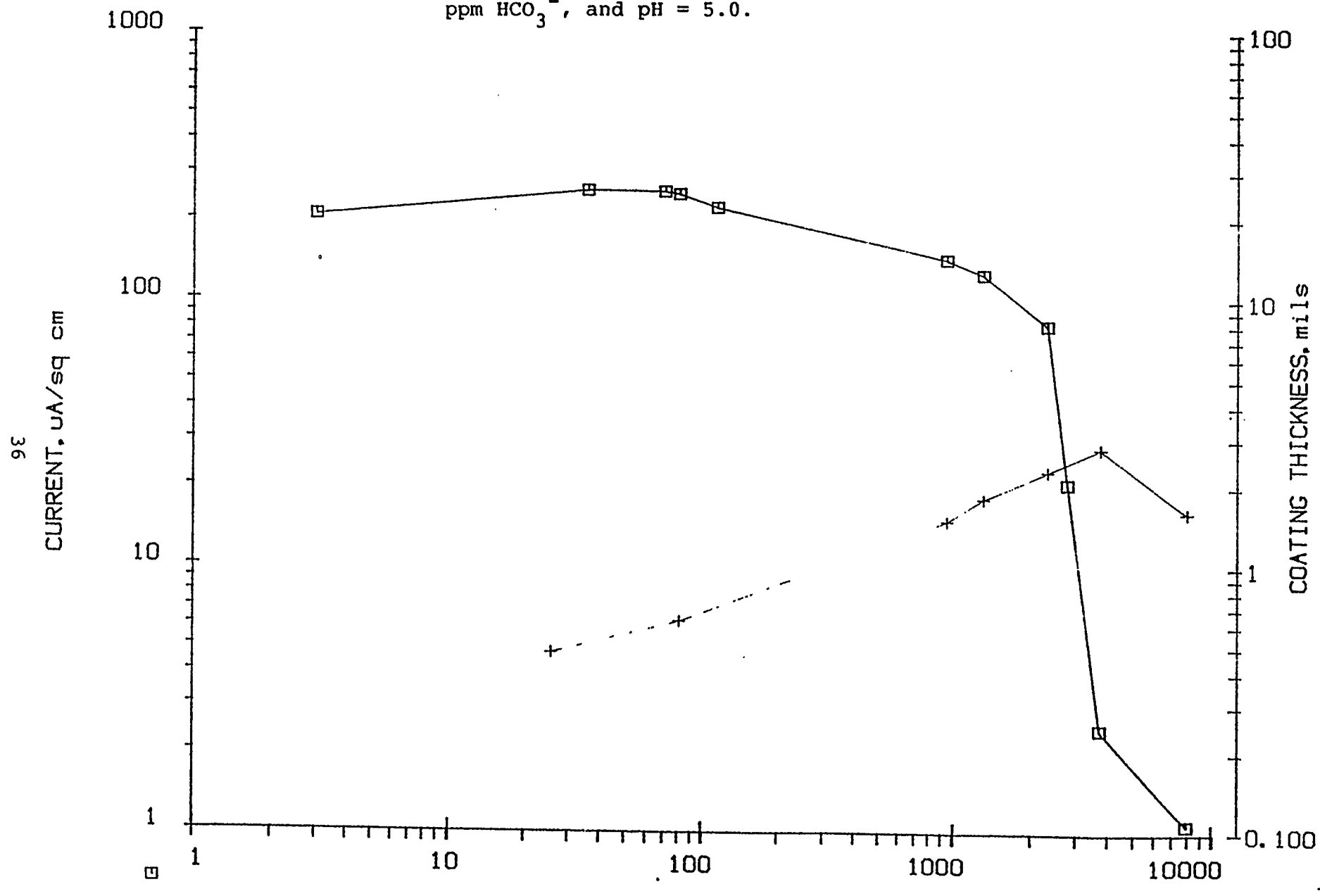
Considering the above-described results, further tests were conducted investigating additional solution modifications that would possibly enhance the calcite deposition/growth process. Since the calcite deposition/growth process under the subject conditions is triggered by a pH gradient at the solution/substrate interface, it was reasoned that lowering the bulk solution pH would create a steeper pH gradient and ultimately promote a thicker film. As a result, tests at $\text{pH}=3.5$ and $\text{pH}=5.0$ were carried out. The test coupons were maintained at a constant potential of -1.05 volts. The test at $\text{pH}=3.5$ produced only a few scattered crystals on the coupon surface after 24 hours. However, in the test with a bulk solution $\text{pH}=5$, a thin uniform coating developed. Figure 16 shows the appearance at 18 hours.

Given the promising initial results of the $\text{pH}=5$ test, film thickness/cathodic current vs. time plots were then developed over a longer period (≈ 7 days) in the same solution. Figure 17



FIGURE 16 - SEM Photomicrograph of the Surface of a 1 cm² Steel Coupon Held at -1.05 Volts vs. SCE for 18 Hours in a Solution of 500 ppm Ca⁺⁺, 150 ppm HCO₃⁻, and pH = 5.0 (300X).

FIGURE 17 - Crystal Layer Thickness and Cathodic Current Versus Time Plots for a 1 cm² Coupon Held at -1.05 Volts vs. SCE in a Solution of 500 ppm Ca⁺⁺, 150 ppm HCO₃⁻, and pH = 5.0.



presents these results. The coating grew to approximately 3.2 mils before the current began to decrease sharply. With the sharp decrease in current, the coating thickness also began to decrease. It is believed that with the sharp decrease in current, the pH gradient disappeared so that the calcite coating was exposed to approximately the bulk solution pH (5) in which calcite would be expected to dissolve. Figure 18 shows the appearance of the test coupon after 5.5 days.

An attempt was then made to restimulate film growth on the coupon used in above-described experiment by placing the coupon in a solution having similar Ca^{++} and HCO_3^- concentrations (500 and 150 ppm, respectively) but with a bulk pH of 7.8. The coupon potential was also increased to -1.30 volts, causing a corresponding increase in cathodic current density from 5 $\mu\text{A}/\text{cm}^2$ to 100 $\mu\text{A}/\text{cm}^2$. This approach, however, was not successful. Hydrogen gas evolution occurred on the surface and disrupted the coating (Figure 19).

A slightly different approach was then investigated. It was reasoned that perhaps a thick coating with hydrogen-caused voids could be produced at a high current density and that these voids could be filled in at a lower current density. A test coupon was exposed in calcite solution (500 ppm Ca^{++} , 150 ppm HCO_3^- , pH=7.8) initially at a potential of -1.2 volts (high current) for 4 days to build a thick coating (along with the voids caused by hydrogen gas evolution.) The potential was then made less negative (-1.05 volts, minimizing hydrogen gas evolution) in order to fill the voids created by gas evolution at the more negative potential. Figure 20 shows the surface appearance after 4 days at high current (=500 $\mu\text{A}/\text{cm}^2$) and Figure 21 shows the coupon after the subsequent 4-day exposure to a lower current density (=40 $\mu\text{A}/\text{cm}^2$). The resulting coating exhibited nonuniform surface coverage (thick in some places, thin in others) and was quite brittle.



FIGURE 18 - Appearance of Test Coupon after 5.5 Days Immersion in a Solution of 500 ppm Ca^{++} , 150 ppm HCO_3^- , and pH = 5.0 at a potential of -1.05 volts vs. SCE.

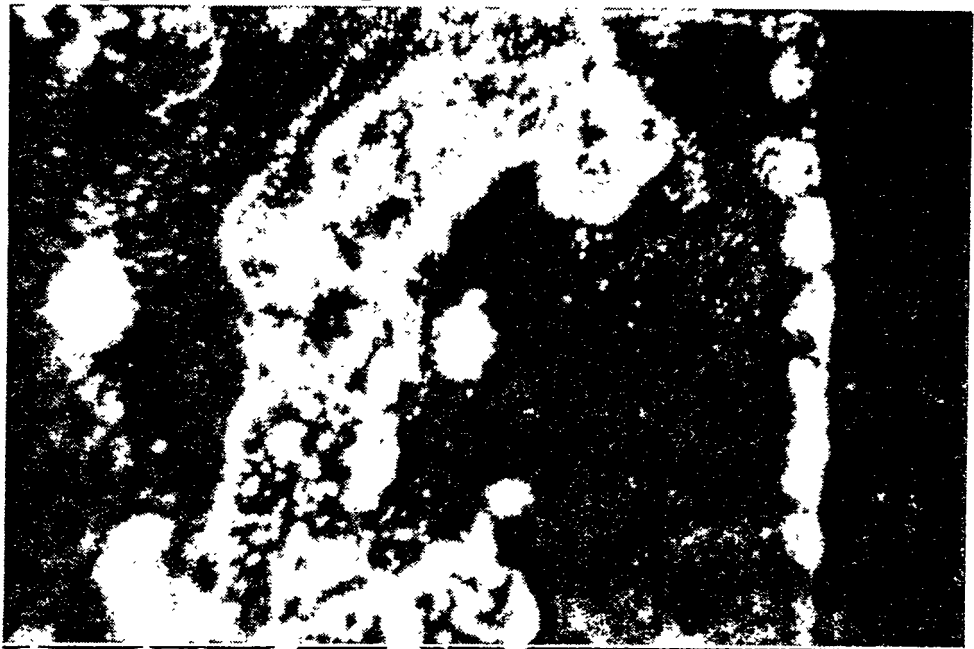


FIGURE 19 - Disruption of the Coating Due to Hydrogen Gas Evolution on the Test Coupon Surface after Reexposure for 21 Hours at a Potential of -1.3 volts vs. SCE in a Solution of 500 ppm Ca^{++} , 150 ppm HCO_3^- , and pH = 7

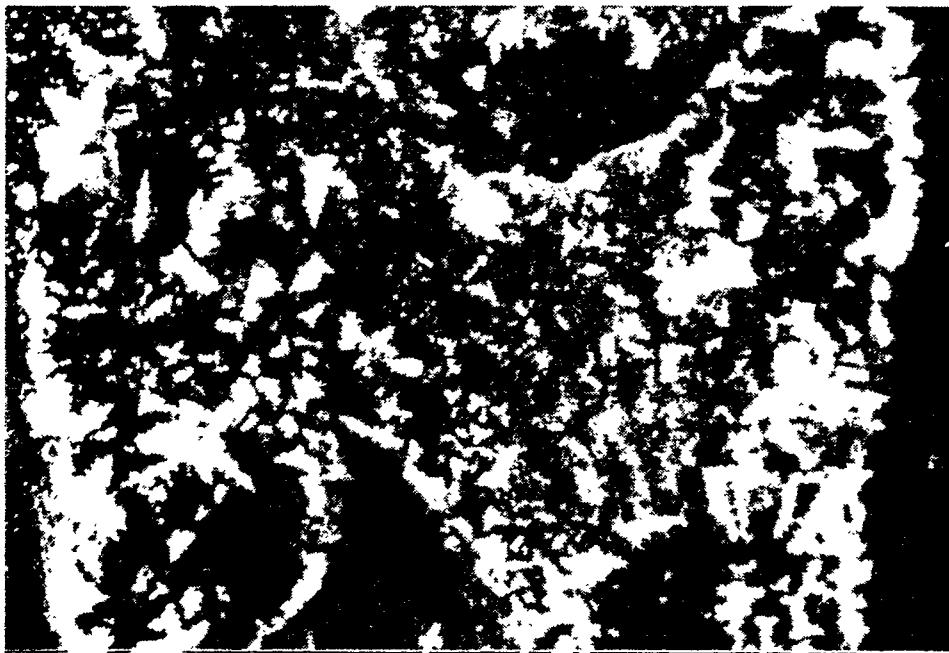


FIGURE 20 - Surface Appearance of Test Coupon Held at -1.2 volts vs. SCE for Four Days in a Solution of 500 ppm Ca^{++} , 150 ppm HCO_3^- , and pH = 7.8.



FIGURE 21 - Surface Appearance of Test Coupon Shown in Figure 20 after Continued Exposure at a Less Negative Potential of -1.05 Volts for 4 Days.

Again, based on the somewhat promising results of the tests employing a bulk solution pH of 5, another test was conducted investigating the possible benefits of increasing the Ca^{++} concentration, so as to increase the supersaturation ratio at the metal interface. The initial test solution at pH=5 had a Ca^{++} concentration of 500 ppm. However, in acidic solutions virtually all of the carbonate is in the form of bicarbonate so that significantly more Ca^{++} can be dissolved in the solution. As a result, a coupon was immersed in a test solution of 5000 ppm Ca^{++} , 150 ppm HCO_3^- , pH=5 and held at a potential of **-1.05 volts** for 2.5 days. The results, however, were not significantly different than those observed at the lower Ca^{++} concentration (500 ppm Ca^{++}). Figure 22 shows the appearance of the surface as observed with a scanning electron microscope.

At this point, the benefits of slight solution agitation in combination with the improved solution chemistry/cathodic current approach were investigated. A test coupon was exposed in 500 ppm Ca^{++} , 150 ppm HCO_3^- , pH=7.8 solution at a constant potential of -1.05 volts, with the test solution slightly stirred using a magnetic stirring bar. A hard, tenacious coating developed on the coupon in 3 days, with a thickness approaching 12 mils at the peaks (Figure 23). These results are substantially different than those obtained under similar conditions without the solution stirring -- where the development of the coating was slower, less uniform, and less adherent. It is also noteworthy that the above-described solution is significantly less supersaturated than those used in the rotating disk experiments. Test coupons immersed under identical conditions including the stirring but without the applied cathodic current developed no coating, demonstrating the importance of the cathodic current in this particular deposition scheme.

Another experiment also demonstrated the ability of cathodic current to enhance the deposition process under the right conditions. A thin calcite film was deposited on a 3" x 5"

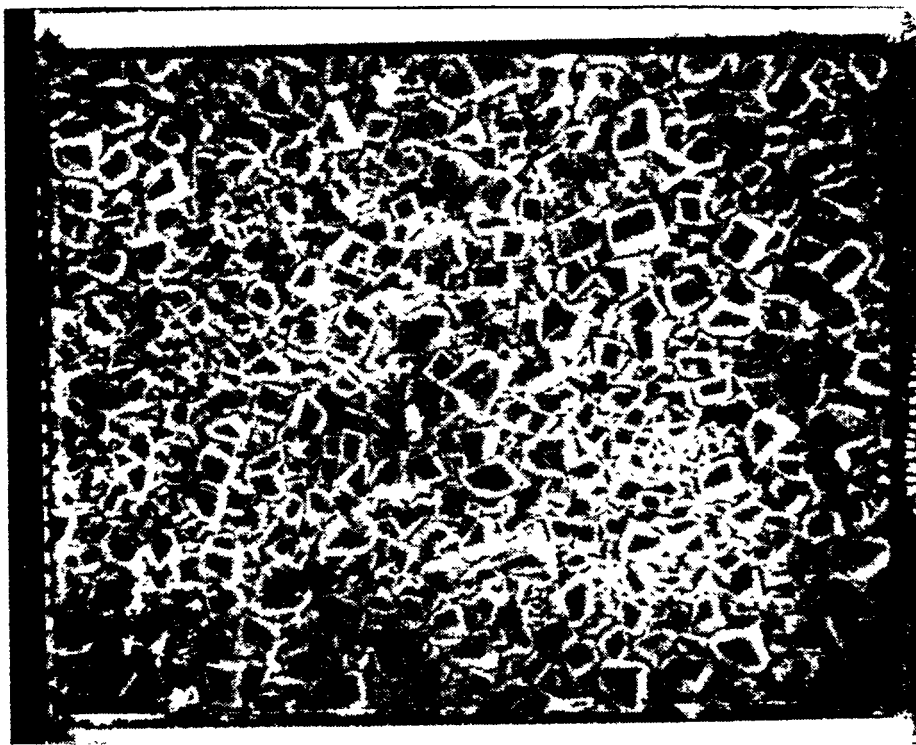


FIGURE 22 - SEM Photomicrograph of Surface Area on Coupon Held at -1.05 Volts vs. SCE for 2½ Days in a Solution of 5000 ppm Ca^{++} , 150 ppm HCO_3^- , and pH = 7.8 (300X).



FIGURE 23 - Surface Appearance of Test Coupon Held at -1.05 Volts vs. SCE for 3 Days in a Stirred Solution of 500 ppm Ca^{++} , 150 ppm HCO_3^- , and pH = 7.8.

Q-panel using the solution chemistry/cathodic current described previously. Subsequently, this panel as well as an uncoated control panel were suspended in an agitated, highly supersaturated solution without cathodic current. The panel on which a thin film had first been deposited evidenced adherent, closely packed crystal growth while the control panel evidenced no crystal growth and simply rusted.

A final set of tests was conducted to evaluate the electrical characteristics of the calcite coating developed using a modified solution chemistry versus the calcite-like coating developed in natural seawater. Test coupons were immersed in both natural seawater and a solution of 10,000 ppm Ca^{++} , 150 ppm HCO_3^- , and pH=7.8. The test coupons were coupled to zinc anodes. After 3 weeks, the coating which developed in the modified solution exhibited an electrical resistance **versus a resistance of $\leq 50 \Omega \cdot \text{cm}^2$** for the coating developed in natural seawater. In general, a higher electrical coating resistance is indicative of a more protective coating.

In addition to the zinc-coupled coupon mentioned above, a magnesium-coupled coupon was also exposed in the modified solution. This coupon developed a comparatively thick film (=80 roils) over the same time frame. However, the electrical resistance of the film measured only **$1500 \Omega \cdot \text{cm}^2$ versus $67,000 \Omega \cdot \text{cm}^2$** for the thinner film developed on the zinc-coupled coupon. These results suggest that the protective nature of the calcite film cannot be judged solely by thickness.

SECTION 5
Summary and Recommendations
For Future Work

SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

As in the initial study, the laboratory tests in the subject program demonstrated that solution flow/agitation beneficially affects the calcite coating process. More importantly, however, the subject study demonstrated that with an appropriate modification of calcite solution chemistry, cathodic current could be used to trigger deposition of uniform, well-bonded, comparatively thin calcite films in a quiescent situation. In the earlier study, attempts to promote or enhance the calcite deposition process using cathodic current were unsuccessful.

Furthermore, the results of the present study suggest that comparatively thick, well bonded calcite films might be developed in a reasonable time frame by using a less saturated, lower pH solution chemistry in combination with cathodic current and slight to moderate agitation. It appears that the agitation required will be substantially less than is required to develop a calcite coating by strict chemical deposition from a highly supersaturated solution as traditionally done in the waterworks industry. For segregated ballast tanks, a high level of solution agitation comparable to that required for strict chemical deposition is thought to be impractical given the geometry of the tank construction and relative inaccessibility. However, the level of agitation that is required using the modified approach might be practically achievable in segregated ballast tanks.

Based on the modified approach of calcite coating deposition, the initial results appear promising and encourage further work in this area. The further work should include:

- (1) Characterization of cathodic current/agitation methods that might be adaptable to the ballast tank situation (e.g. the Butterworth spray equipment used for cleaning ballast tanks might be used to provide the necessary agitation).

(2) Demonstration of the actual corrosion protection afforded by various coating techniques.

SECTION 6

References

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2. R. F. McCauley and W. O. Abdullah, "Carbonate Deposits for Pipe Protection", Vol. 50, November, 1958.